

# Geophysical Research Letters

## RESEARCH LETTER

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### Key Points:

- Microseismic events result in pH drops of 1–3 units for <24 h in groundwater in silicic rocks
- Experiments fracturing granodiorite and quartz in synthetic groundwaters replicate the observed pH drop
- pH drops are due to the silica radicals and silanols formed at the slip plane

### Supporting Information:

- Supporting Information S1
- Data Set S1

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## Microseismic Events Cause Significant pH Drops in Groundwater

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**Abstract** Earthquakes cause rock fracturing, opening new flow pathways which can result in the mixing of previously isolated geofluids with differing geochemistries. Here, we present the first evidence that seismic events can significantly reduce groundwater pH without the requirement for fluid mixing, solely through the process of dynamic rock fracturing. At the Grimsel Test Site, Switzerland, we observe repeated, short-lived groundwater pH drops of 1–3.5 units, while major and minor ion groundwater concentrations remain constant. Acidification coincides with reservoir drainage and induced microseismic events. In laboratory experiments, we demonstrate that fresh rock surfaces made by particle cracking interact with the in situ water molecules, likely through creation of surface silanols and silica radicals, increasing the H<sup>+</sup> concentration and significantly lowering groundwater pH. Our findings are significant; pH exerts a fundamental control on the rate and outcome of most aqueous geochemical reactions and microseismic events are commonplace, even in seismically inactive regions.

**Plain Language Summary** Earthquakes can change groundwater composition by opening new fractures, mixing different water sources. In this paper, we describe observations of changes in water pH from small earthquake events triggered by the drainage and refilling of a reservoir. The reservoir overlies a tunnel system created for underground research at Grimselpass, Switzerland. The rocks are cut by several open fractures which transport surface or reservoir water into the tunnels, and which are long enough to have hosted small earthquakes. Tiny earthquake events caused no changes in groundwater pressure or chemistry, but resulted in groundwater locally becoming significantly more acidic (equivalent to the difference between tapwater and vinegar). To explain this observation, we conducted experiments to grind and break rock fragments in water of similar chemistry to the water at Grimsel. The first experiments ground particles and the second experiments broke rock fragments, using a hydraulic press. Both experiments confirmed that reactions between water and fresh mineral surfaces can make water more acid. Small earthquakes are common in the Earth's crust, even in areas that do not regularly experience large earthquakes. Our results suggest that in silica rich rocks, short-term acidification of groundwater may arise as a result of cracking, due to small earthquakes.

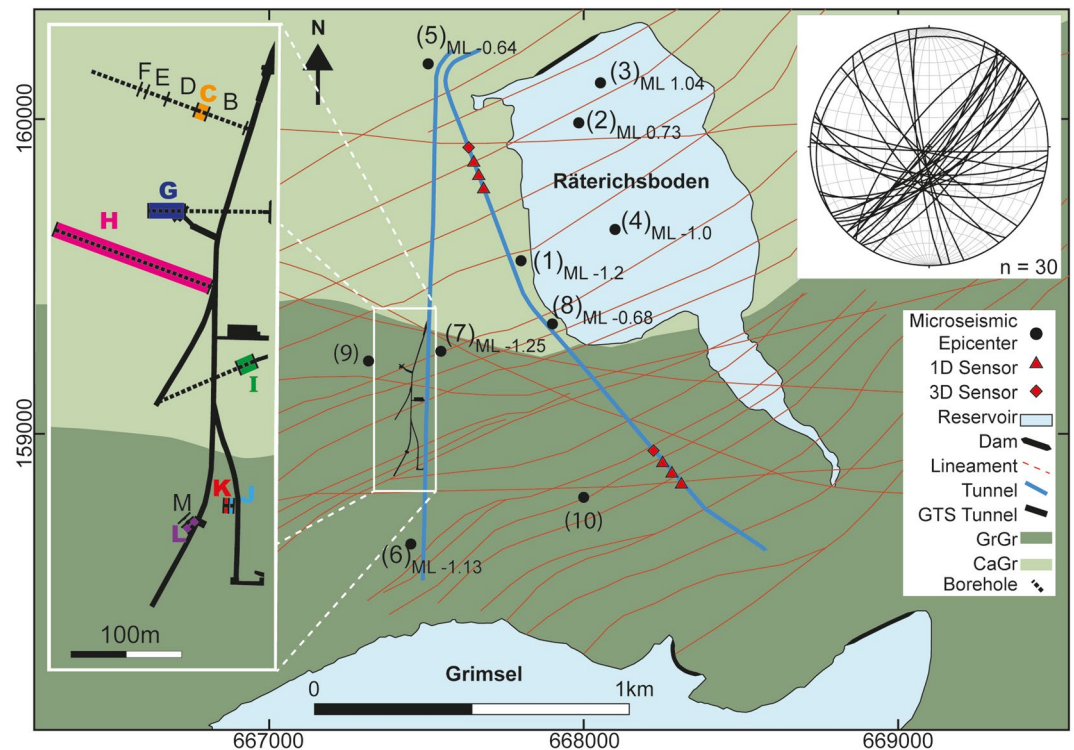
## 1. Introduction

Fracturing during earthquakes can alter groundwater hydrogeochemistry: postseismic observations reveal significant changes to the permeability and connectivity of regional flow networks (Brodsky et al., 2003; Fischer et al., 2017), expressed as increases in gas discharge rates (CO<sub>2</sub> [Cappa & Rutqvist, 2012; Sulem & Famin, 2009], H<sub>2</sub> [Sato et al., 1986], <sup>222</sup>Rn and <sup>3</sup>He/<sup>4</sup>He [King et al., 2006]) and isotope anomalies from the tapping of isotopically different groundwater sources (Onda et al., 2018; Skelton et al., 2014). These impacts occur because during earthquakes, existing fractures are propagated or reactivated, and new ones created, that act to “tap” or mix distinctly different, previously isolated groundwater bodies (Skelton et al., 2014). To-date, such observations have been associated with events of magnitude (M<sub>L</sub>) over 3.5 (Fischer et al., 2017). Gas expulsions have also been observed due to similar processes (Fischer et al., 2017).

Here, we show that microseismic events can cause changes to in situ groundwater pH, of 1–3 units, and that these pH changes are caused by the dynamic fracturing process itself and not by the mixing of previously isolated, geochemically distinct groundwaters. We present observations, from the Grimsel Test Site (GTS) in Switzerland, of groundwater pH fluctuations that are concurrent with nearby shallow (<1 km below

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**Figure 1.** Map of the Grimsel Test Site (GTS) local coordinate system LV95. Red lines show mapped surface lineaments (Schneeberger et al., 2017b), solid blue and black lines represent access and GTS tunnels, respectively. Microseismic epicenters (black circles) are chronologically numbered and labeled with the local magnitude ( $M_L$ ) where possible. The main map shows the lithological contact between Aar Granite (light-green) and Grimsel Granodiorite (dark-green) at the surface. The enlarged GTS map (inset left) shows the contact at 1,728 m AMSL and the boreholes (dashed black line) and sampling intervals B to K. Intervals with a pH change (C, G, H, I, K, J, L) are colored to match the key in Figure 3. The stereonet shows orientations of open fractures in the GTS (Schneeberger et al., 2017a) and other tunnels.

ground surface) microearthquakes  $M_L < 1$  (and as low as  $-1.2M_L$ ). These pH changes are not accompanied by changes in water pressure or other water chemistry parameters, and hence cannot be explained by a mechanism of groundwater mixing. We conduct experiments to crush granodiorite from the GTS in the presence of equilibrated groundwater. These experiments produce similar pH drops with no other change in the water chemistry, consistent with our field observations. The drops occur due to the creation of fresh rock surfaces containing silanols and silica radicals (Saruwatari et al., 2004) that, in the absence of oxygen, interact with the in situ water molecules, increasing the relative concentration of  $H^+$  and lowering the pH: thus, the fracturing process itself has a direct effect on pH. pH exerts a fundamental control on the rate and outcome of most aqueous dissolution reactions and microseismic events that could create such pH changes are commonplace even in seismically inactive regions. Hence, our findings have significant implications for understanding the temporal and spatial evolution of groundwater geochemistry and in situ water-rock interactions.

## 2. Field Site

We monitored groundwater chemistry and microseismic activity at the GTS during two periods (Nov 2014; Feb 2016) during which the neighboring Lake Räterichsboden reservoir (Figure 1) was drained and refilled. The GTS is a series of tunnels hosted in fractured Central Aar Granite (CAGr) to the North and Grimsel Granodiorite (GrGr) to the South (Figure 1). Groundwater flow in the CAGr and the GrGr occurs primarily within brittle open fracture systems and fault zones; the host rocks have very low porosity 0.8–1.53 vol.% (Bossart & Mazurek, 1991). These fractures were formed during the later brittle activation of ductile shear zones (Challandes et al., 2008; Wehrens, 2015). Alpine tectonic deformation occurred in two main phases; (1) Handegg phase resulting in SE dipping shear zones, (2) Oberaar phase resulting in strike slip and oblique

slip, forming E-W, NW-SE, and NNE-SSW striking ductile shear zones (Schneeberger et al., 2016; Wehrens, 2015). Ductile shear zones form the precursor structures to later brittle overprinting and fracture formation. The fractures and faults have been shown to extend from the surface to the depth of the GTS (Schneeberger et al., 2017a).

Stable isotope measurements ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$  values) confirm a meteoric groundwater source (Schneeberger et al., 2017b) within the fracture network that cuts the GTS tunnels. Chemical modeling shows groundwater chemistry is in equilibrium with the host rock, reflecting localized water-rock interaction (Schneeberger et al., 2017b). Groundwater flow in the region is topographically driven from infiltrating meteoric water and penetrates to the depth of the GTS.

### 3. Field Observations

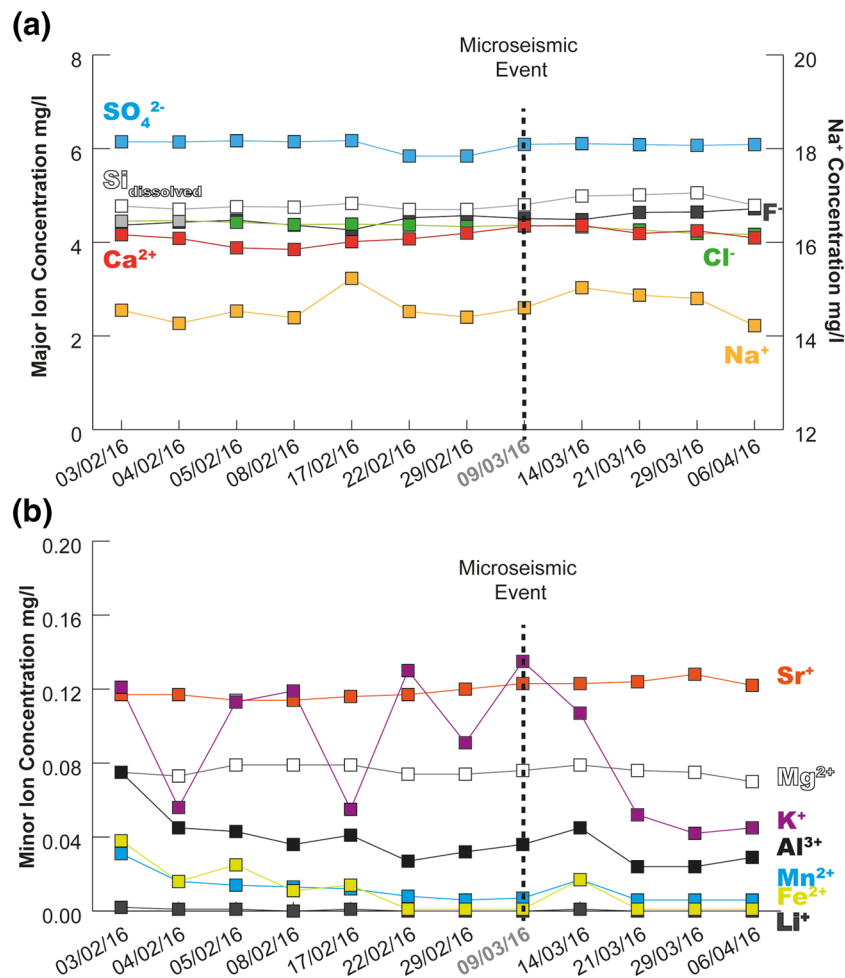
To monitor microseismic events induced during the reservoir drainage and refilling periods (see Figure S1), two surface microseismic arrays were deployed in late 2014 within a tunnel that lies between the GTS and Lake Räterichsboden (Figure 1). Each array consists of one 3-component and three vertical component short-period seismometers. The first array was  $\sim 1$  km to the East of the GTS, the second  $\sim 1$  km to the North, both at an average depth of 120 m below surface at a similar elevation to the GTS. The sampling rate was 250 Hz (for further microseismic methodology see Text S1, supporting information).

To explore the potential influence of lake drainage on the groundwater chemistry regular groundwater samples were taken from the GTS. These samples were collected from fractures cutting 12 packed borehole intervals (marked B-M, Figure 1). During the first drainage period (Nov-2014) groundwater sampling was weekly, during the second period (Feb-2016) sampling was daily during drainage and weekly thereafter. Sampling took two forms. First, in situ measurements were taken using a flow-through cell at the borehole headworks to measure flow rate, pH ( $\pm 0.2$  units), Eh ( $\pm 20$  mV), conductivity ( $\pm 0.5\%$  of reading), temperature ( $\pm 0.1^\circ\text{C}$ ) and dissolved oxygen ( $\pm 2\%$  of reading). Second, water samples were pretreated and preserved according to the methodology in Text S2 (supporting information), with samples collected for analysis of  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ ,  $\text{Si}_{\text{diss}}$  for cations,  $\text{NO}_3^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  for anions and alkalinity.

#### 3.1. Groundwater Geochemical Observations

Background groundwater chemistry was characterized using all samples taken during this study. As expected, the mean groundwater physiochemistry and dissolved ion chemistry show a slight spatial difference between the northern and southern boreholes in the GTS, reflecting the difference in lithology (Schneeberger et al., 2016, 2017b). The mean pH is 9.0 and 9.4 for groundwater in the CAGr and GrGr, respectively. These relatively high pH values evolve due to water-rock reactions. Based on  $\delta^{18}\text{O}$  and  $\delta\text{D}$  stable isotope values, and tritium measurement, groundwater is meteoric in origin and takes  $\sim 65$  years to reach the GTS (Schneeberger et al., 2017b). Over the two sampling periods in 2014–2015 and 2016 we find no significant variations in the mean or variance of dissolved ion chemistry, electrical conductivity, groundwater flow rate, or groundwater temperature. An example of the typically limited temporal fluctuation in ion concentrations is given for borehole “I” in Figures 2 and S2).

By contrast to the dissolved ion chemistry, significant variations in pH occur in a number of boreholes during both drainage periods (Figure 3). Short-lived ( $< 24$  h) pH drops in individual boreholes reach values that lie far outside the baseline pH for each rock type. The short-term pH drops are observed in several, but not all, of the borehole intervals (Figure 3); drops are on different days for different intervals (each of which cut different fractures). In Nov-2014, two of seven borehole intervals (c) and (h) in the North of the GTS (Figure 3a) experience pH drops of 0.6 and 2.1 units respectively, and four of five Southern intervals are affected (Figure 3b). In Feb-2016, similar behavior is observed, this time in two monitoring intervals in the South, I and K (Figure 3d), and in one original and three new intervals (C, B, E, and G) in the North (Figure 3c). Interval “I” experienced particularly large pH drops: 1.5 units (11/02/16) and 3.3 units (09/03/16). All the



**Figure 2.** (a) Major ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Si}^{\text{dissolved}}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ )  $\text{Na}^+$  plotted on secondary y-axis (right) and (b) minor ( $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{K}^+$ ,  $\text{Li}^+$ , and  $\text{Sr}^+$ ) dissolved ion concentrations for borehole interval “I” over the 2016 sampling period where the largest pH change of 3 units was detected on the 09/03/16 (black dashed line), note that the date axis does not reflect the time between sampling and instead reflects the order in which the samples were taken.

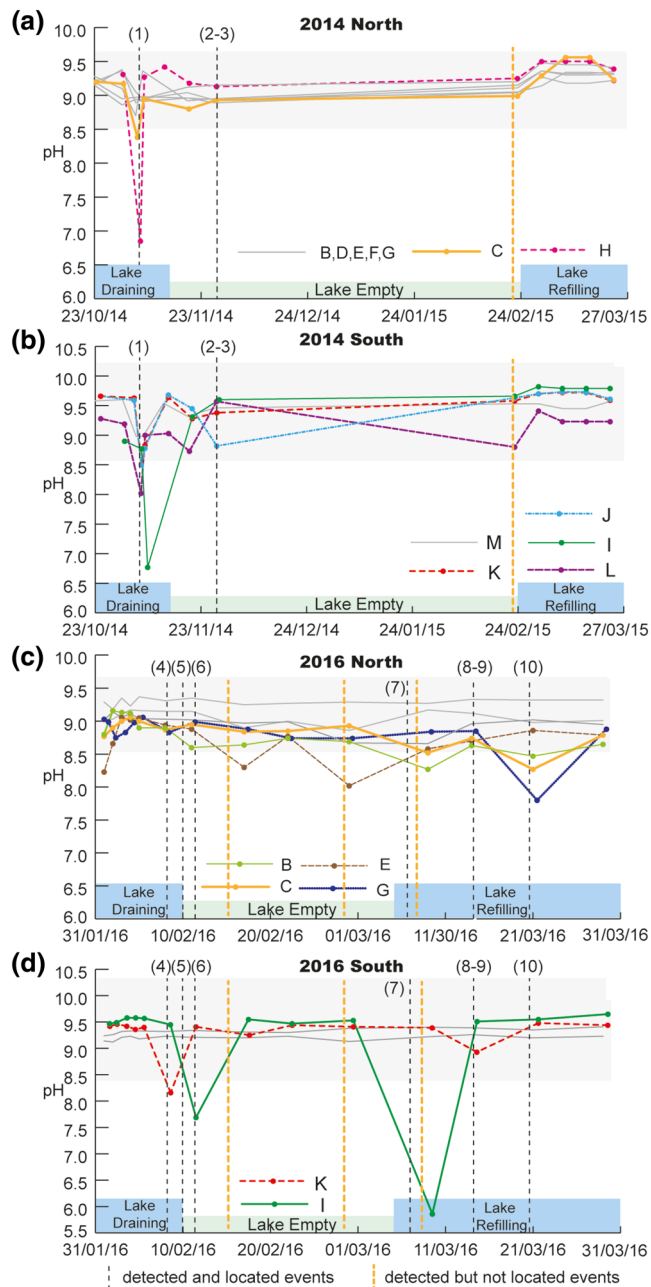
observed pH drops are short-lived, recovering to background levels by the following measurement; implying that pH recovers in 24 h or less.

### 3.2. Microseismic Observations

We scanned the 48-h period preceding each pH drop (Figure 3) for any seismic events, naturally occurring or triggered by the reservoir drainage and refilling. The timings of all detected events within a 2 km radius of the GTS (as determined by the difference between the P-wave and S-wave arrival times) are shown on Figure 3. All pH drops are preceded by at least one event. Figure 1 shows the epicenters of all of the locatable events marked on Figure 3. Events that were not locatable were either not detected by a sufficient number of sensors, or occurred so close to the sensors that the sampling rate was insufficiently high to distinguish the p-wave arrival times between individual sensors.

The local magnitudes for the events in Figure 1 were between  $-1.2$  and  $1 M_L$  following the formula in Fäh et al., 2011 for local magnitudes in Switzerland. Using Brune's model (Brune, 1970), the estimated slip patch fracture surface areas for these events are  $1,300\text{--}6,350 \text{ m}^2$ . Surface lineaments (Schneeberger et al., 2017a) indicate the presence of two main fractures sets, striking NE-SW and NW-SE (Figure 1), that are of sufficient lateral extent they could host microseismic events of this magnitude (12–100 m fault length; Zoback





**Figure 3.** Groundwater pH measurements during periods of reservoir drainage. Lines with markers show pH in borehole intervals colored to match locations in Figure 1, dark gray lines denote boreholes with no detectable change. Graphs are separated by year and host rock lithology; (a and c) come from the Aar Granite whereas (b and d) are sampled in the Grimsel granodiorite. The gray shaded area shows 95 percentiles for background pH. Located microseismic events corresponding to the numbered epicenters in Figure 1 are denoted by vertical black dashed lines. Unlocated events are vertical yellow dashed lines.

& Gorelick, 2012). The persistence of these two dominant fracture sets at depth is supported by observations in the GTS tunnels and boreholes (stereonet Figure 1).

## 4. The Relationship Between Microseismicity and pH

There are three well-documented mechanisms that could potentially explain a link between microseismicity and transient changes to pH. These are as follows: (i) Rock grinding along slip surfaces, exposing fresh surface area for mineral dissolution, thus changing the groundwater chemistry and lowering the pH; (ii) The influx of a pulse of lower pH water due to a transient change in the fracture flow network during the microseismic event; (iii) The generation of a groundwater pressure pulse, caused by the microseismic event, that causes a transient shift in the  $\text{CO}_2$ -carbonate equilibrium (Pytkowicz, 1963) in the groundwater, forcing an increase in the concentration of carboxylic acid and, hence, a drop in pH (Culberson & Pytkowicz, 1968).

### 4.1. Rock Grinding

Chemical kinetic modeling by Schneeberger et al. (2017b) shows that, for the minerals in the GTS host rocks, water-rock reactions as a result of mineral dissolution on fresh fracture surfaces would result in an increase in groundwater pH rather than the observed significant pH decrease. Further, chemical speciation calculations (Schneeberger et al., 2017b) show that the groundwater at the GTS is close to, or in, equilibrium with the major minerals present within both the CAGr and the GrGr. Hence, no further significant dissolution should occur.

### 4.2. Groundwater Mixing

For larger magnitude seismic events investigated elsewhere (e.g., Yechieli & Bein, 2002), hydrogeochemical changes are attributed to “tapping” and mixing of distinct groundwater bodies by coseismic fracture network opening. Documented water bodies in the GTS region are groundwater of meteoric origin (Schneeberger et al., 2017b), surface water (lake and rainwater), and deep thermal waters, each with a distinct dissolved ion geochemistry (Waber et al., 2017). No changes in dissolved ion chemistry were associated with the pH drops (Figures 2 and S2), nor were there any detectable changes in groundwater pressure (Figure S4). Hence, there is no evidence for mixing or “tapping” of other water sources.

### 4.3. Carbonate-Bicarbonate Equilibrium

Transient groundwater pressure changes could shift the  $\text{CO}_2$ -carbonate-bicarbonate equilibrium, potentially generating carboxylic acid, leading to a decrease in groundwater pH. This effect was explored through equilibrium calculations, carried out in PHREEQC (Parkhurst & Appelo, 2013) using the reaction pressure data block, (Figure S3) at varying pressures to emulate an in situ pressure rise generated by a micro-

seismic slip event. Seismically induced groundwater pressure changes have been observed at other sites, the 2011 Tohoku Earthquake caused a groundwater head increase of 15 m (Niwa et al., 2012) corresponding to a pressure rise of  $\sim 10$  kPa. A similar head rise of 15 m at the GTS would correspond to a predicted pH drop of

<0.001 units (based on CO<sub>2</sub>-carbonate-bicarbonate equilibrium calculations): well below the measurement error of pH at the GTS and hence would not be observable. Furthermore, pressure rises were not detected in any of the sampling intervals (Figure S4), in fact the only pressure changes observed were small pressure drops, due to the removal of water samples for the geochemical analyses. Hence, there is no evidence for pressure changes causing the observed pH drops at the GTS.

#### 4.4. Laboratory Experiments

None of these well-documented mechanisms relating seismic events to changes in pH provide a plausible explanation for the observed short-lived, 1–3.5 unit pH drops at the GTS. However, a small number of laboratory studies, which largely focus on determining planetary mechanisms for hydrogen gas generation, have shown that fracturing of silicic rocks leads to the splitting of siloxane bonds. During splitting, if the electrons are split evenly between the Si and the O, this results in the formation of surface radicals, whereas if the split is such that both electrons are taken by the oxygen, charged Si<sup>+</sup> and SiO<sup>−</sup> surface species are formed (Saruwatari et al., 2004). On reaction with pure water, the surface species form stable silanol groups and release hydrogen ions into solution, resulting in a decrease in pH:

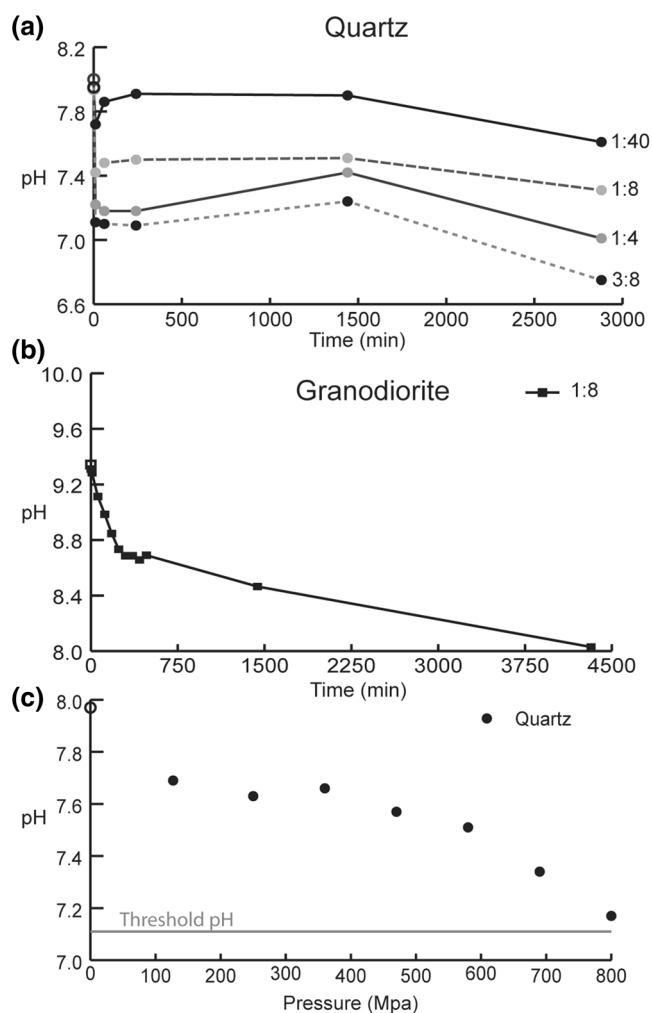


Studies have hypothesized that this mechanochemical reaction could result in the production of hydrogen gas from large magnitude earthquakes (Kita et al., 1982; Sato et al., 1986; Wakita et al., 1980) and from subglacial rock comminution (Telling et al., 2015). In these studies, laboratory experiments have been conducted exploring mechanochemical hydrogen production by crushing rock grains with deionized water (Kameda et al., 2003; Telling et al., 2015). One study showed that a change in pH occurs in deionized waters (Saruwatari et al., 2004).

To explore whether mechanochemical reactions could be responsible for the drops in pH observed at the GTS, we conducted three sets of laboratory experiments. Experiment 1 used a ball mill to grind quartz (the most common silicate mineral), adding between 1 and 15 g of quartz sand to 40 g of synthetic GTS groundwater (equilibrated with crushed Grimsel granodiorite until there was no change in solution pH), to explore the temporal effect on pH of increasing the “freshly fractured” surface area. Ball mills achieve grain size reduction through ball-grain-mortar impacts that crack the grains, and by grain-grain surface abrasion. Experiment 2 used a ball mill to grind rock fragments derived from rocks at the GTS with and without oxygen present (representing near-surface oxygenated and subsurface deoxygenated fracturing conditions, the latter was the only experiment conducted under argon). Both experiments used 1.25 g of crushed granodiorite with 10 g of synthetic groundwater. Experiment 3 was designed to explore the effect of the grain fracturing process: tests were conducted using a hydraulic press (as opposed to the ball mill) to fracture the grains without the secondary process of surface abrasion. Grain fracturing occurs within the press by increasing the in situ fluid pressure within a rigid uniaxial cell (Hutchison et al., 2015), thus simulating fresh crack propagation. All samples were composed of 2 g of quartz sand, mixed with 2 g of synthetic groundwater and tests were conducted using hydraulic pressures between 0.1 and 0.8 GPa. In the sealed uniaxial cell pH could not be monitored over time, so all measurements were taken 1 h after peak hydraulic pressure was reached. Additional information on experimental conditions and methods are presented in the supporting information (Text S3).

In Experiments 1 (Quartz) and 2 (Granodiorite; Figure 4), we observed in situ pH drops (instrument accuracy  $\pm 0.06$ ) that increased from 0.3 to 0.9 units as the quartz-to-groundwater mass ratio increased from 1:40 to 3:8, respectively (Figure 4a). That is, with more quartz grain crushing, the magnitude of the pH drop increased. In Experiment 2 (Figure 4b) with the granodiorite, a drop of 1.3 units occurred over a period of 66 h, but only when conducted under argon. In Experiment 3, increasing the hydraulic pressure used for grain cracking in the cell results in a more significant drop in the final pH, which ranges from 0.3 to 0.8 (Figure 4c), reflecting the increase in fractured surface area. A comparison of Experiment 3 (ratio of 1:1 w:w) with the closest test in Figure 4a (ratio of 3:8 w:w) shows that the drop in pH is greater in the hydraulic press.

These experiments, alongside past studies (Saruwatari et al., 2004), demonstrate that mechanical activation of mineral surfaces is a viable mechanism to explain the short-lived 1–3.5 unit pH drops observed in the GTS



**Figure 4.** (a, b) Quartz and granodiorite grain crushing and (c) hydrostatic fracturing experiments using synthetic groundwater. Experimental results showing evolution of pH as a result of grain crushing with different mass ratios of rock to water (1:40, 1:8, 1:4, and 3:8). (a) quartz and (b) pH evolution with time for granodiorite grains crushed in granodiorite-equilibrated water under an argon atmosphere. (c) The effect on pH of hydrostatic grain fracturing at increasing pressures. Hydrostatic fracturing of quartz sand grains shows increasing pH change with pressure. Measurements of pH taken 10 min after uniaxial cell reaches the desired pressure. Gray line labeled “Threshold pH” shows the pH threshold for ball-mill-crushed Quartz after 10 min for a rock to water mass ratio of 3:8 at atmospheric pressures.

groundwaters. Further, increasing the ratio of cracked mineral grains to in situ groundwater increases the size of the pH drop.

## 5. Discussion

Our observations suggest that in situ groundwater pH drops occur due to mechanochemical reactions on the fractured surface of slipped patches, during microseismic events. This low pH groundwater then propagates from the event location, through the local fracture network, to the monitoring boreholes. The speed of propagation may be enhanced by an in situ pressure rise caused by the slip event (Pytharouli et al., 2011), which would act to increase the hydraulic gradient between the event and the monitoring boreholes. Laboratory results indicate that pH drops are long-lived and then the observed return to background pH in the borehole, within 24 h, is likely due to the pulse of high pH water continuing to propagate past the borehole interval rather than the pH itself returning to background levels. Ultimately, however, the pulse of low pH water will recover to background levels via diffusion of the affected water over time.

The observed temporal variability in pH drops between individual boreholes, and indeed between adjacent monitoring intervals in the same borehole, implies that while regionally connected, individual fractures are locally hydraulically isolated from each other, as is common in fracture-dominated flow systems (Birgersson et al., 1993). This focusing of groundwater flow within a few individual channels will tend to preserve the pH peaks, rather than rapidly disperse them. Further, the variations in the magnitude of the pH drop associated with individual events, likely reflects the variations in individual microseismic event magnitudes; these are directly related to the size of the slipped patch and thus to the extent of fresh fracture surfaces created and abraded during slip.

pH exerts a fundamental control on the rate and outcome of most aqueous geochemical reactions. If this process of microseismically driven short-term pH drops is a common occurrence, it could have important implications for understanding water-rock interactions in silicic rocks. For example, pH plays a vital role in chemical weathering of the subsurface in alpine areas, with a reduction in pH being associated with increased dissolution of Ca and Mg from minerals in the continental crust: Experimental results show a two unit drop in pH can increase Mg and Ca dissolution of diopside by ~70% and ~50%, respectively (Golubev et al., 2005). Traditionally, the frequency of occurrence of seismic events is predicted using the standard Gutenberg-Richter frequency-magnitude (GRF) distribution (Gutenberg & Richter, 1994) which predicts that event frequency should logarithmically increase with decreasing event magnitude. Microseismic event frequency is rarely quantified, since magnitude 2 is the lowest complete magnitude ( $M_c$ ) threshold (detection threshold)

of most permanent seismic networks. However, one study shows that the GRF distribution remains applicable for small events (Abercrombie & Brune, 1994) and, by implication, that microseismic events are very common on geological timescales. For example, the GRF would predict over 17 million earthquakes of magnitude  $-1$  or above with slip patches  $> 1,200 \text{ m}^2$  in area every thousand years in the UK, which is tectonically quiescent, and over 2 billion in Switzerland. Hence, localized temporal pH drops within groundwater, and their associated effects on in situ rock-water geochemical interactions, may be common even in tectonically quiescent areas. These findings have further implications, as the same reactions are associated with seismogenic  $\text{H}_2$  gas production essential for metabolic activity in the subsurface (McMahon et al., 2016). Seismogenic  $\text{H}_2$  gas production was previously associated with large magnitude seismic events

(McMahon et al., 2016). Our results indicate that  $H_2$  generation in faults and fractures could be much more commonplace than initially thought.

## 6. Conclusions

We have presented the first field evidence to show that microseismic events in silicic rocks are associated with mechanochemical reactions that cause significant drops in in situ groundwater pH. We report groundwater monitoring data from the GTS in Switzerland, where, temporal, groundwater pH fluctuations are concurrent with nearby shallow ( $<1$  km below ground surface) microearthquakes  $M_L < 1$  (and as low as  $-1.2M_L$ ). We observe repeated, short-lived, pH drops of 1–3.5 units that are not accompanied by changes in groundwater pressure, nor in the concentrations of major or minor ions, all of which remain unchanged. Previously reported mechanisms relating earthquakes to changes in groundwater chemistry cannot explain the magnitude of the observed pH drops. Through laboratory experiments, we demonstrate that the creation of fresh rock surfaces made by mineral fracturing and abrasion, lowers the groundwater pH. We suggest this occurs through the creation of surface silanols and silica radicals which interact with the in situ water molecules thereby increasing the concentration of  $H^+$  in solution. pH exerts a fundamental control on the rate and outcome of most aqueous geochemical reactions and microseismic events are commonplace, even in seismically inactive regions. Hence, our findings can have significant implications for understanding the temporal and spatial evolution of groundwater geochemistry and in situ water-rock interactions.

## Data Availability Statement

Data are available from the University of Strathclyde KnowledgeBase at <https://doi.org/10.15129/971b80a9-27b1-4dac-bbbb-b9aaf2051b65>.

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